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# Response to "Comment on: Corrected Debye-Hückel theory of electrolyte solutions"

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(Received 3 August 1983; accepted 13 September 1983)

The relationship between the corrected Debye-Hückel (CDH) theory and the many alternative theories of electrolytes is described in greater detail elsewhere.<sup>1</sup> The agreement of the linear but nonlocal GvdW-CDH equation for the charge density with an equation arising from the Kirkwood fluctuation analysis<sup>2</sup> is worthy of particular attention since, as noted by Outhwaite above, several approximate solutions of this nonlocal equation have been obtained. They could be incorporated into the GvdW-CDH theory. The simpler CDH theory now under discussion differs from preceding methods based on Kirkwood's analysis in many important respects. The thermodynamic properties are obtained by charging a hard sphere fluid in the GvdW (I) approximation. The hard sphere correlation correction to the electrostatic energy is obtained in a local approximation incorporating charge density inhomogeneity by a moment expansion method. The ionic atmospheres are calculated by perturbation theory valid in the low concentration limit. The charge density retains Debye-Hückel form but the Debye length is renormalized. At higher concentrations the CDH theory, like the Debye-Hückel theory, amounts to a successful ex-

trapolation. The moment expansion method for the correlation correction breaks down most obviously because the charge density has a step function nonanalyticity at  $r = d$  where hard sphere repulsion drops  $\rho(r)$  to zero. It is possible to calculate the correlation correction exactly (i.e., without the use of a moment expansion) for atmospheres of Debye-Hückel form. This has been done<sup>1</sup> in a variational calculation which yields an optimized Debye-Hückel charge density. The CDH theory is seen to overestimate  $\kappa$  at higher concentrations but due to the increasingly dominant hard sphere effects the thermodynamic properties remain in reasonable agreement. The onset of charge density oscillations is neglected in both forms of CDH theory. This reflection of correlation nonlocality is important as are effects due to number density oscillation and nonlinearity which have also been neglected. Their relative strengths remain to be explored in detail.

<sup>1</sup>S. Nordholm, Aust. J. Chem. (to be published).

<sup>2</sup>J. G. Kirkwood, J. Chem. Phys. **2**, 767 (1934); Chem. Rev. **19**, 275 (1936).

## ERRATA

### Erratum: Quantum dynamics of the van der Waals molecule (N<sub>2</sub>)<sub>2</sub>: An *ab initio* treatment [J. Chem. Phys. **77**, 5664 (1982)]

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The action of the permutation-inversion operators on the body-fixed coordinates and, consequently, on the basis functions used in this paper has been given incorrectly. This also led to an incorrect assignment of the symmetry labels (the irreducible representations of the group  $S_4' \otimes C_i$ ) to the calculated ro-vibrational states. In order to obtain the correct results one has to interchange the permutation-inversion operators in Tables I and II as follows:

$$P_{13,24} \leftrightarrow P_{14,23}^*,$$

$$P_{14,23} \leftrightarrow P_{13,24}^*,$$

$$P_{1324} \leftrightarrow P_{1423}^*,$$

$$P_{1423} \leftrightarrow P_{1324}^*,$$

and the labeling of the (odd) states throughout the paper as

$$A_1^- \leftrightarrow B_2^-,$$

$$A_2^- \leftrightarrow B_1^-.$$

The dipole selection rules (Sec. VII A) are correct, but the symmetry relation (32) for the dipole expansion coefficients with respect to interchange of  $L_A$  and  $L_B$  should read

$$m_{L_A, L_B, L, K} = (-1)^{L+1} m_{L_B, L_A, L, K}.$$

The first allowed  $A_1^+ \leftrightarrow B_1^-$  and  $A_2^- \leftrightarrow B_2^+$  transitions from the vibrational ground state in *ortho-ortho* complexes (Sec. VII B) lie at 22.2 and 24.9 cm<sup>-1</sup>, while the results given for the  $E^+ \leftrightarrow E^-$  transitions in *ortho-para* complexes are still valid.

We are grateful to Geert Brocks for drawing our attention to this error.